

# PATENT SPECIFICATION

600,999

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## PROVISIONAL SPECIFICATION

### Printed Sheet Materials

We, WILLIAM ELLIOTT FREW GATES, of 38, Attimore Road, Welwyn Garden City, in the County of Hertford, a British Subject, and IMPERIAL CHEMICAL INDUSTRIES 5 LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention to be as follows:—

This invention relates to the production 10 of printed sheet materials which contain polythene, the normally solid polymers of ethylene, as their major ingredients.

Sheets of materials which consist of, or 15 are based on, polythene are of utility because of their extremely low moisture permeability, because of their resistance to attack by chemical reagents and solvents and because of their excellence as electrical insulators. Sheets of these 20 materials have been found, however, to be difficult to print.

According to the present invention we have now found that satisfactory printed 25 sheets of materials which contain polythene as their major ingredient may be obtained by printing with printing mixtures of dyes and/or pigments and materials which are capable of forming solid solutions with polythene when the 30 materials of the sheets are molten and supported by a backing, said printing mixtures having softening points less than the temperature of the molten material of the sheet.

35 Materials which are capable of forming solid solutions with polythene include polystyrene; hydrogenated polystyrene; polythene; waxes obtained by the pyrolysis of polythene; chlorinated polythene; 40 polyisobutylene; rubber, cyclised rubber; synthetic rubbers as "Neoprene, G.R.S." and butyl rubber; gutta percha; gum elemi; ester gum; hydrogenated ester gum; hydrogenated oils, such as hydrogenated castor oil; waxes such as paraffin or micro-crystalline wax or ozokerites, carnauba, ceresin, montana, Halowax (Registered Trade Mark) or bees wax; chlorinated naphthalenes and diphenyls;

asphalts; polypropylene; polypropylene sebacate and polyvinyl isobutyl ether. The preferred dyes for use in the process of this invention are wax soluble dyes such as "Waxoline" (Registered Trade Mark) dyes. Dyes and/or pigments may be mixed into the printing mixtures by grinding or preferably, malaxating. Many of these printing mixtures are and may be applied to printing plates or rollers by pressing them on at normal temperatures. Others should be softened by heat or a solvent for polythene such as liquid hydrocarbons or chlorinated hydrocarbon, for ease of application to printing plates or rollers.

A sheet of material to be printed by the process of this invention may be supported on a backing consisting of a fibrous material, such as paper or fabric, the sheet of material printed forming a strongly adherent coating on the fibrous material. Alternatively the sheet of material to be printed may be supported on a polished metal surface so that it may be stripped from the surface when cooled to the solid state. Such polished metal surfaces may form the surface of a roller or a continuous band if continuous operation is proposed. These polished metal surfaces may be coated, if desired, with a separating aid, such as a high melting point grease; aluminium or zinc stearate; or a glazing material such as sodium silicate or a detergent of the type sold under the name "Vulcastab C" (Registered Trade Mark) or "Lissapol C" (Registered Trade Mark).

It is preferred that the means for applying the printing materials of this invention to the sheets to be printed should be cooled so as to chill the sheets printed from the molten to the solid state. This results in a sharp impression of the design printed onto the sheet and rapid chilling improves the gloss of the surface of the sheet.

The sheets of material may be in the molten state immediately after, or during

formation or may be heated to the molten state prior to printing. Thus sheets of polythene foamed as coatings on sheets of fibrous material by the process of British 5 Application No. 25682/45 may be printed by applying the printing mixtures of this invention to the coatings before they have cooled from the molten state, the sheet of fibrous material forming the backing of 10 this invention. Also sheets formed by the process of British Specification 567,358 may be printed during their formation, one or both of the cold surfaces used for chilling the polymer rapidly being used 15 as a means for applying the printing mixtures, one or both of these surfaces being used as the backing. Alternatively, prior to printing, sheets of materials which contain polythene as their major 20 ingredient may be heated to the molten

state by such means as hot rollers or infra heating units when the sheets are backed, e.g., by fibrous materials to which they will adhere tenaciously after cooling or by the polished metal surfaces of rollers 25 or continuous bands from which they may be stripped after cooling. Heating sheets of material which contain polythene as their major ingredient to the molten state has the advantage that any pin-holes 30 which may be present in these sheets after their formation will tend to disappear. However, if the sheets prior to heating contain molecules oriented in a particular direction, the sheets will shrink on themselves in the line of orientation when melted.

Dated the 7th day of December, 1945.

E. A. BINGEN,  
Solicitor for the Applicants.

## COMPLETE SPECIFICATION

### Printed Sheet Materials

We, WILLIAM ELLIOTT FREW GATES, of 38, Attimore Road, Welwyn Garden City, 40 in the County of Hertford, a British Subject, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, London, S.W.1, a British Company, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the production 50 of printed sheet materials which contain polythene, the normally solid polymers of ethylene, as their major ingredients.

Sheets of materials which consist of, or are based on, polythene are of utility 55 because of their extremely low moisture permeability, their resistance to attack chemical reagents and solvents and their excellence as electrical insulators. Sheets of these materials have been found, however, to be difficult to print.

According to the present invention we have now found that satisfactory printed sheet of a material which contains polythene as its major ingredient may be obtained by a process which comprises printing a sheet of said material while it is molten and supported by a backing with a printing mixture of one or more dyes and/or pigments and a material which is capable of forming a solid solution with polythene, said printing mixture having a softening temperature which is a lower than the temperature of the molten material of said sheet.

It is preferred that the sheet be cooled rapidly from the molten state to the solid state immediately after printing, since

this results in the formation of a sharp impression of the design printed on to the sheet and an improvement in the gloss of the surface of the sheet. This cooling step is preferably carried out by cooling the means for applying the printing mixtures to the molten sheet. For example the printing mixture is conveniently applied by means of a printing plate or roller, and these may also serve to chill the sheet from the molten to the solid state.

Materials which are capable of forming solid solutions with polythene include polystyrene; hydrogenated polystyrene; polythene; waxes obtained by the pyrolysis of polythene; chlorinated polythene; polyisobutylene; rubber; cyclised rubber; synthetic rubbers such as "Neoprene", "G.R.S." and butyl rubber; gutta percha; gum elemi; ester gum; hydrogenated ester gum; hydrogenated oils such as hydrogenated castor oil; waxes such as paraffin or micro-crystalline wax or ozokerites, carnauba, ceresin, montana, Halowax (Registered Trade Mark) or bees wax; chlorinated naphthalenes and diphenyls; asphalts; polypropylene; polypropylene sebacate and polyvinyl isobutyl ether. The preferred dyes for use in the process of this invention are wax soluble dyes such as "Waxoline" (Registered Trade Mark) dyes. Dyes and/or pigments may be mixed into the printing mixtures by grinding or preferably by malaxating. Many of these printing mixtures may be applied to printing plates or rollers by pressing them on at normal temperature. Others should be softened by heat or a solvent for polythene, such as a liquid

hydrocarbon or chlorinated hydrocarbon, for ease of application to printing plates or rollers.

The sheet of material to be printed by the process of this invention may be supported on a polished metal surface so that it may be stripped from the surface when cooled to the solid state. Such polished metal surfaces may form the surface of a roller or a continuous band if continuous operation is proposed. These polished metal surfaces may be coated, if desired with a separating aid, such as a high melting point grease; aluminium or zinc stearate; or a glazing material such as sodium silicate or a detergent of the type sold under the name "Vulcastab C" or "Lissapol C" (Registered Trade Marks). Alternatively, the sheet of material to be printed may be supported on a backing consisting of a fibrous material, such as paper or fabric, the sheet of material printed forming a strongly adherent coating on the fibrous material.

The sheets of material may be in the molten state immediately after or during formation, or may be heated to the molten state prior to printing. Thus sheets of polythene formed as coatings on sheets of fibrous material by the process of British Application No. 25682/45 (Serial No. 600,687) may be printed by applying the printing mixtures of this invention to the coatings before they have cooled from the molten state, the sheet of fibrous material forming the backing which supports the molten sheet. Also sheets formed by the process of British Specification 567,358 may be printed during their formation, one or both of the cold surfaces used for chilling the polymer rapidly being used as a means for applying the printing mixtures, and one or both of these surfaces being used as the backing. Alternatively, sheets of materials which contain polythene as their major ingredient may be heated to the molten state before printing by such means as hot rollers or infra red heating units, while the sheets are supported by a backing, for example, by fibrous materials to which they will adhere tenaciously after cooling, or by the polished metal surfaces of rollers or continuous bands from which they may be stripped after cooling. Heating sheets of material which contain polythene as their major ingredient to the molten state has the advantage that any pin-holes which may be present in these sheets after their formation will tend to disappear. However, if the sheets prior to heating contain molecules oriented in a particular direction, the sheet will shrink on themselves in the line of orientation when melted.

Our invention is illustrated but in no way limited by the following example, in which all parts given are by weight.

#### EXAMPLE.

A mixture containing 20 parts of "Alkathene" (Registered Trade Mark) Grade 700, 10 parts of ester gum, 15 parts of polyisobutylene (molecular weight 8000), 5 parts of microcrystalline wax (melting point 140—145° F.) and 1.5 parts of "Waxoline" (Registered Trade Mark) Yellow dye 1.5, was heated until it was molten and was then stirred with 100 parts of xylene to form a homogeneous paste. This paste was used to ink a roller made from "Wolvic" (Registered Trade Mark) which bore a printing design in relief on its surface. This roller rotated in contact with a cold steel roller on to the surface of which the inked design was transferred. The steel roller further contacted the "Alkathene" surface of a sheet of "Alkathene" coated paper while the coating was still molten, and thus printed and chilled the "Alkathene" coating simultaneously. This process resulted in the formation of a sharp impression of the design of the "Wolvic" roller on the surface of the coated sheet material.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:

1. A process for the production of printed sheet of a material which contains polythene as its major ingredient which comprises printing a sheet of said material while it is molten and supported by a backing with a printing mixture of one or more dyes and/or pigments and a material which is capable of forming a solid solution with polythene, said printing mixture having a softening temperature which is lower than the temperature of the molten material of said sheet.

2. A process according to claim 1 in which said sheet is cooled rapidly from the molten to the solid state immediately after printing.

3. A process according to claim 2 in which said sheet is cooled by cooling the means for applying said printing mixture to said sheet, for example a printing plate or roller.

4. A process according to any of the preceding claims in which said dyes are wax-soluble dyes.

5. A process according to any of the preceding claims in which said sheet is supported while it is molten by a polished metal surface, for example, the surface of a metal roller or endless metal band, and

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- is stripped from said surface when it has cooled to the solid state.
6. A process according to any of claims 1 to 4 in which said sheet is supported by 5 a backing consisting of a fibrous material, such as paper or fabric, said sheet forming a strongly adherent coating on the fibrous material when it is cooled to the solid state.
- 10 7. A process for the production of printed sheet of a material which contains

polythene as a major ingredient substantially as hereinbefore described with reference to the foregoing example.

8. Printed sheets, including coatings 15 on sheets of fibrous materials, of materials containing polythene as their major ingredients whenever produced by the process of any of the preceding claims.

Dated the 6th day of December, 1946. 20

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